HARDNESS AND YOUNG'S MODULUS OF NICKEL COATINGS PRODUCED FROM EMULSION OF Sc-CO_2 ESTIMATED BY NANOINDENTATION

Md. Ziaur Rahman[1], **Masato Sone**[2], **Masao Eguchi**[1], **Koji Ikeda**[1], **Seizo Miyata**[2] **and Takashi Yamamoto**[1]

[1] Department of Mechanical Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei-shi, Tokyo 184-8588, Japan.
[2] Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei-shi, Tokyo 184-8588, Japan.

ABSTRACT
Nanoindentation has been used extensively for characterization of mechanical properties of materials in small scales and thin films. In this study, nanoindentation tests were done to estimate the hardness and Young's modulus of electroplated nickel (Ni) coating films deposited on brass substrate in a wide range of indentation forces (10mN-400mN). The electroplated Ni coating film was produced from an emulsion of supercritical carbon dioxide (Sc-CO_2), electroplating solution and nonionic surfactant. The indentation load-displacement behavior was tested with a Berkovich indenter. The morphology of nickel coating films and their properties were investigated by using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). It was found that nickel coating films produced from emulsion of Sc-CO_2 have higher hardness (30%) and stiffness (10%) than that of produced with conventional electroplating system. Restriction to dislocation motion of Ni film would makes coating film harder and coating film's low rigidity was resembled with amorphous metals like behavior.

Keywords: Nanoindentation, Nickel film, Electroplating.

1. INTRODUCTION
Nanoindentation is a common test method in characterization of mechanical properties of thin coatings, films and advanced micro devices. Nano- and micro-scale tribology plays a prominent role in many emerging fields, such as microelectromechanical systems (MEMS) [1]. Moreover, hard coatings with potential stiffness are capable of improving the tribological performance and service lifetimes of macro and micromahcine components. Various MEMS devices such as pressure sensors, thermal actuators, microcoils, micromotors and microstructures based on plated metals have been fabricated and studied [2-3]. The electroplating is one of the most economic processes for applying metallic coatings to many engineering components. Electroplated metal thin films comprising nickel (Ni) and nickel-iron (NiFe) are commonly used for MEMS as they provide a simple and cheap technology with superior material properties and device performances.

In addition, electroplated coatings are employed in industry to improve appearance of surfaces, to give good corrosion protection of the substrate, to improve wear resistance by hard facing of the relatively soft substrate, and sometimes to provide good electrical and thermal contacts [4]. With the increasing concern over toxic wastes produced by conventional metal finishing operations, there is a strong need to replace 'dirty' electroplating processes with 'clean' technologies. In the quest of improved nickel coatings films, a number of works [5-8] had been done to produce a new environmentally friendly technology for industrial application using supercritical CO_2 (Sc-CO_2) as a reaction medium. This new nickel films have a higher uniformity, a smaller grain size, and a significantly higher Vickers hardness (680 Hv) and its wear properties were evaluated by pin on plate tribometer [9].

In the present study, an attempt was taken to identify the surface hardness (*H*) and Young's modulus (*E*) of nano-structured Ni thin layered coating surface which was produced on brass substrate from emulsion of supercritical carbon dioxide by applying a nano-indenter. The nanoindentation results were analyzed and compared with conventionally electroplated nickel coating film.

2. EXPERIMENTAL DETAILS

2.1 Materials and Method
The emulsion was produced by a) the electroplating solution, referred to as a "modified Watts bath",

consisted of nickel sulfate (372g/l), nickel chloride (88g/l), boric acid (95g/l), saccharin (3g/l) and 1, 4-butynediol (0.5g/l), b) octa (ethylene oxide) dodecyl ether ($H(OCH_2CH_2)_8O(CH_2)_{12}H$) nonionic surfactant, and c) 99.9% pure carbon dioxide.

Fig 1 shows the high-pressure experimental apparatus (reaction cell). A typical electroplating reaction was performed in a constantly agitated ternary system of Sc-CO_2, electroplating solution and surfactant. The reaction cell was kept in a temperature-controlled air bath with magnetic stirrer to keep particles from sediment. The anode was a pure nickel (purity 99.9%) plate of 10×20 mm^2. The cathode was a brass substrate of the same size composed of 65.4 mass% of Cu and 34.6 mass% of Zn, with a hardness of 112.7Hv. Both the anode and cathode were attached to the reaction cell using platinum wires and connected to a programmable power source.

Before each reaction, the brass substrate was carefully cleaned with the base and acid solution, and rinsed with de-ionized water. During reaction, the ternary system was agitated at a speed of 400rpm under the constant temperature and pressure with an electric current density of 5.0A/dm^2.

2.2 Electroplating Reaction in Emulsion of Supercritical Carbon Dioxide (Sc-CO_2)

The electroplating reaction was performed at a temperature of 323K and pressure of 10MPa in a constantly agitated ternary system containing 15ml of dense CO_2, and 30ml of the electroplating solution mixed with 1.0% surfactant by weight. Both coating film plated from emulsion of carbon dioxide and conventional plated coating film was produced from 15 minutes of electroplating reaction. Conventional electroplating reaction produces about 3.05±0.1μm of nickel coating film whereas an approximately 1.75±0.05μm thickness

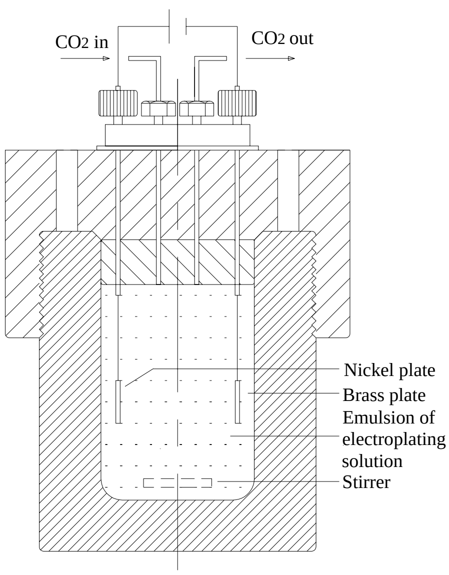

Fig 1. Experimental apparatus used for electroplating reaction with the emulsion of Sc-CO_2, electroplating solution and surfactant

of nickel coating film was produced for the emulsion of Sc-CO_2 electroplating reaction.

2.3 Nanoindentation Test

The Nanoindentation tests were performed using the Berkovich diamond indenter which was pushed into the coating film in nano order. Tests were done three times for each pushing or indentation force. The penetration depth is ideally measured from the level of the sample surface. Hardness (*H*) and Young modulus (*E*) was determined using the Oliver and Pharr approach of analysis [10]. To obtain the nickel coating film nanoindentation data, the tests were performed with a wide range of an indentation depth exceeding 3000 nm.

2.4 Hardness and Young's Modulus

Hardness (*H*) means the resistance to local plastic deformation of materials, which has been conventionally obtained by meaning the projected contact area *A*:

$$H = \frac{P}{A} \tag{1}$$

where *P* is the load of the indenter. Young's modulus (*E*) can be obtained from the contact stiff, using the following relation:

$$S = \frac{2}{\sqrt{\pi}} E\sqrt{A} \tag{2}$$

S is the unloading stiffness which is obtained from the slop of the initial portion of the unloading curve, $S=dP/dh$, where *h* is the indentation depth. The critical indentation depth, h_c can be found by the intersection of slope *S* and the *X*-axis, thereby the contact projection area *A* is computable. Consideration of the form of Berkovich indenter relates the contact projection area *A* with the contact depth h_A:

$$A = 3\sqrt{3}\tan^2 65° h_A{}^2 \tag{3}$$

The following formula can express the contact depth h_A by the maximum indentation depth $h_{\max}$ and h_c:

$$h_A = h_{\max} - 0.75\left(h_{\max} - h_c\right) \tag{4}$$

3. RESULTS

The result of nanoindentation loading-unloading test displacement curves is shown in Fig 2. The Ni plate used for this experiment was 98% pure. This structure of Ni coating film produced from emulsion of Sc-CO_2 was likely to provide substantial resistance to dislocation movement and thus a high hardness it showed which provided lower indentation depth. Moreover, it has been observed that this Ni coating film's apparent hardness was much higher than both conventionally plated Ni film and the bulk hardness of the Ni plate.

A typical indentation force versus indentation depth is shown in Fig 3 where Sc-CO_2 emulsion produced coating film shows lower residual depth value for a wide range of indentation force.

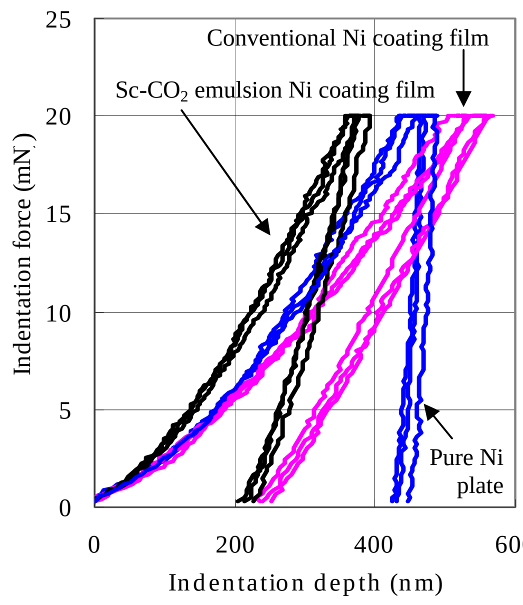

Fig 2. Typical load-displacement curve at low load of 20mN for Ni coating films and Ni plate

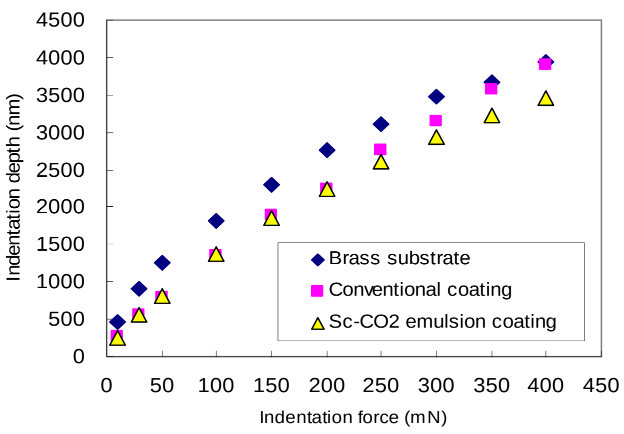

Fig 3. Relationship between indentation force with indentation depth

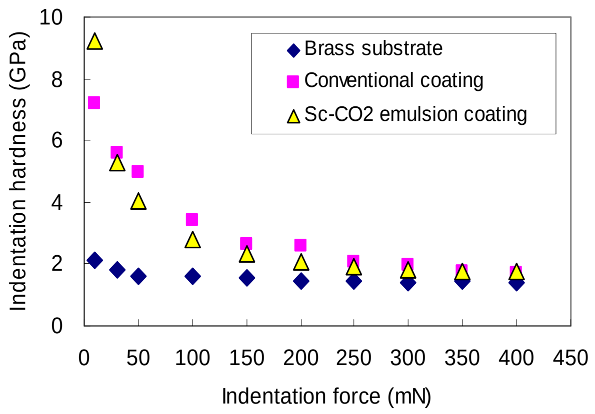

Fig 4. Plot response of hardness value with the indentation force

Fig 4 shows an example of decrease in indentation hardness drastically initially and then in small scale from varying loads of nanoindentation. On the other hand, hardness decreases with increasing indentation depth from the sub-micrometer range towards micrometer range in Fig 5. This decrease in hardness in microscale with an increase in indentation depth could be rationalized on the basis that, as the volume of deformed material increased, there was a higher probability of encountering material defects. Moreover, the observed decrease in hardness might be explained by the influence of the brass substrate on the measured hardness, since the observed hardness of coating films fall towards the hardness of the brass substrate. This influence was profound in Sc-CO_2 emulsion coating film which had two times lower thickness value than that of conventional coating film. However, initially Ni coating film showed a very high hardness value (9.25±1.25 GPa) comparing with the conventional Ni coating film (7.20±0.6 GPa) under 10 mN load.

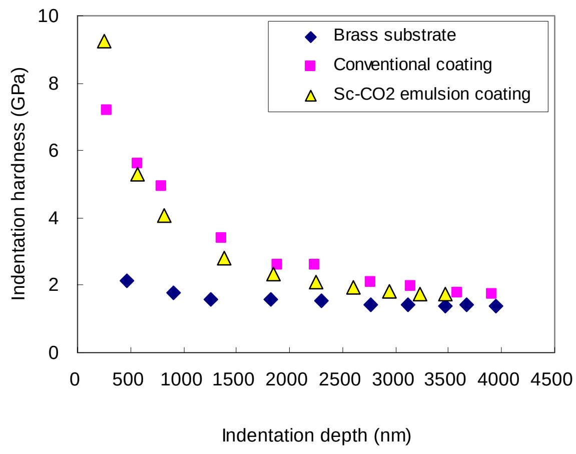

Fig 5. Indentation (penetration) depth dependence on the indentation hardness

Fig 6 is a plot of Young's moduli of two kinds of Ni coating films on brass substrate and brass substrate itself. Though initially under 10 mN load, residual indentation depth for Sc-CO_2 emulsion plated coating film (158.2±13 GPa) was closer to the conventional coating film (146±7 Gpa), it produced very high moduli at higher indentation depth. One possible explanation for this phenomenon is the formation of geometrically necessary dislocations which act as a strengthening mechanism.

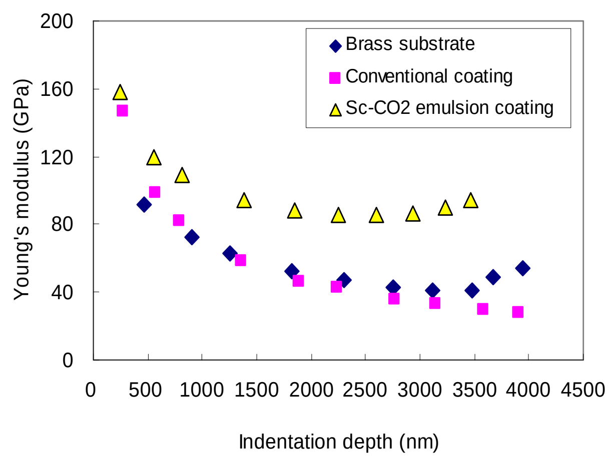

Fig 6. Plot response of Young's modulus value with the indentation depth

4. DISCUSSION

4.1 Deformation Characterization

Now, coating film characteristics could be considered for an extensive nanoindentation loading-unloading tests. For a wide range of loading (in Fig 2 at 20mN and the Fig 7 at 300mN), it showed that the plastic responses of these states of experiment with indentation forces were in similar tendency. The Ni coating film produced with Sc-CO_2 emulsion coating showed lower indentation depth but higher plastic deformation than that of comparing with conventional Ni coating film. This plasticity could be termed as dislocation-mediated plasticity [11] due to small grain size of Ni coating film. From the nanoindentation test with wide range of forces showed that the Sc-CO_2 emulsion plated nickel film have features with high hardness and low rigidity and high stiffness. In addition, being hard, it could be thought that this tendency of low rigidity is resembles with the quality of the amorphous metal. This corresponds with the fact that amorphous adaptation tendency of Sc-CO_2 emulsion coating is high. This feature corresponds to the non crystallization of Sc-CO_2 emulsion produced nano coating. However, there was also an aspect of high deformation resistively too.

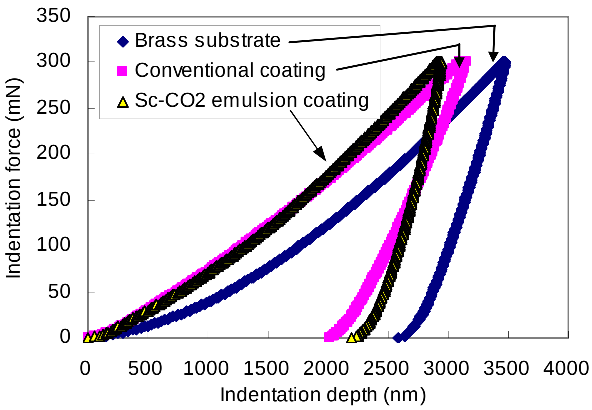

Fig 7. Evidence of plastic response during indentation for a nickel coating on brass substrate system at load 300mN

4.2 SEM and AFM Observations

Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to examine the indentation test evaluating the indentation surface morphologies of Ni coatings and substrate. The Fig 8 shows the topography of indents for uncoated brass substrate and Ni coated films under 300 mN load. The Ni coating film produced with Sc-CO_2 emulsion showed the evidence of little bit wider deformed indent; however, residual depth was smaller than the conventional coating film (see figures correlated with indentation depth). In, AFM results, it (Fig 9a) showed pile-up at high load in case of brass substrate only. Clearly, except the indent of brass, both Ni coating films (Fig 9b, Fig 9c) did not exhibit considerable pile-up or sinking-in effect around nanoindentations.

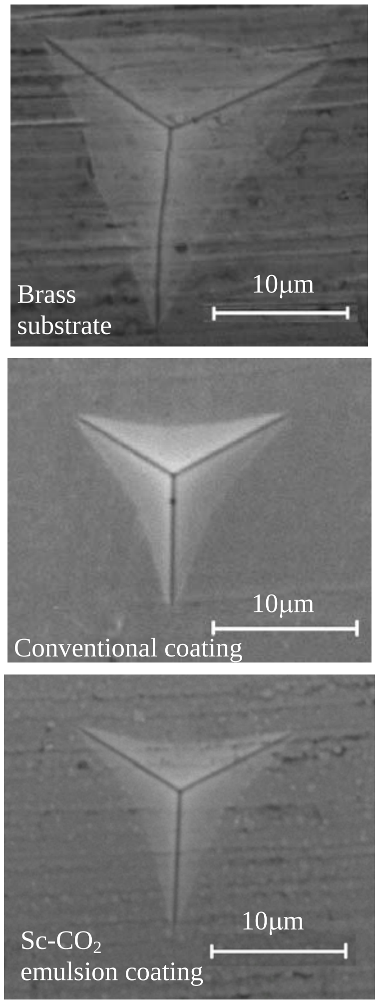

Fig 8. Topology of indents at load 300mN

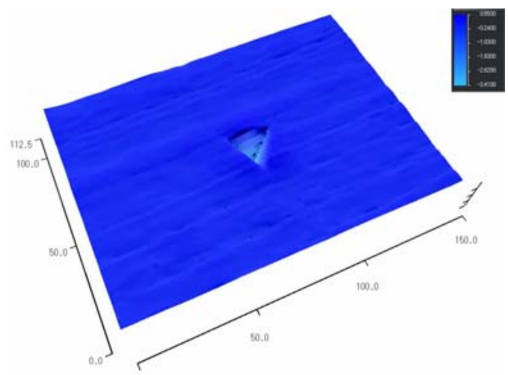

Fig 9a. Brass substrate at load 300mN

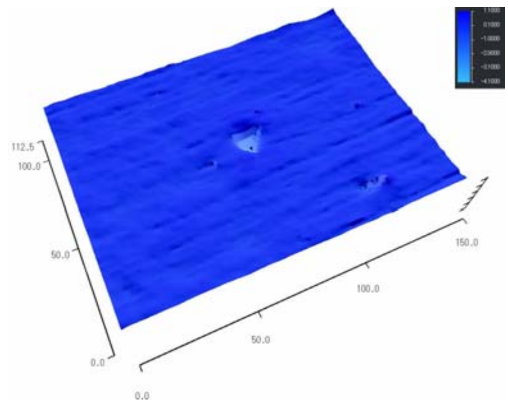

Fig 9b. Conventional coating film at load 300mN

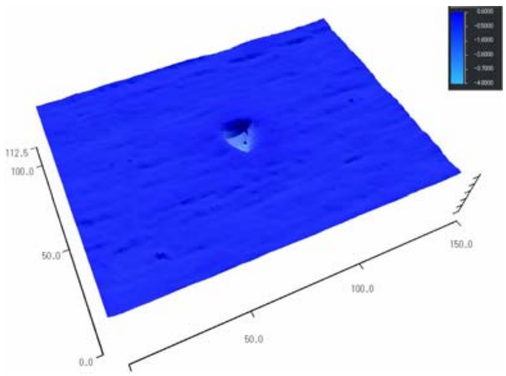

Fig 9c. Sc-CO_2 emulsion coating film at load 300mN

4.3 Strengthening Coating Film by Grain-Size Reduction

It was observed that the grain size of Ni film from the emulsion with Sc-CO_2 was in the range of 10 nm. However, the size of grains of nickel films from the conventional electroplating system was within the range of approximately 22-25 nm [7]. It is known that, the finer the grains, the larger the area of grain boundaries, that impedes dislocation motion. Grain-size reduction usually improves toughness as well. Usually, the strengthening of materials varies with grain size, *d* according to well known Hall-Petch equation:

$$\sigma_y = \sigma_0 + K_y / \sqrt{d} \quad (5)$$

where σ_0 and K_y are constants for a particular material, *d* is the average grain diameter. However, grain size can be controlled by plastic deformation and by appropriate heat treatment. In addition, the fundamental dislocation and grain boundary processes is thought to be responsible for the crossover in the Hall-Petch effect, from ‘normal’ behavior at larger grain sizes to the ‘inverse’ behavior for grain sizes less than typically 20 nm. The more complicated deformation processes controlled by the interplay between dislocation and grain boundary processes that are critical in nanostructurally designed materials. Therefore, it could be said that the increased hardness of the Ni coating film was resulted from the refinement of the grain size.

Now, we can imagine two different metals with different size of grain structure under same indentation loading force. During applied force, when the dislocation reaches the grain boundary, the movement of the grain dislocations stopped. Thus the recovery of the shape becomes difficult and produces plastic deformation. On the process, the materials with large grains have long time till the dislocations are trapped on the grain boundary. Comparing, same load for two kinds of grain size, in the large grains, the dislocations spaces might be left. Thus its grain deformed shape recovery becomes easy. On the case of small grains, the dislocations are easily and quickly trapped on the grains boundary. Therefore, it is suggested that in loading-unloading evidence (Fig 2 and Fig 7) this phenomenon occurs and coating film produced from Sc-CO_2 with smaller grain size shows higher plastic deformation (Fig 8) though it poses comparably lower indentation depth at same indentation force.

5. CONCLUSIONS

The nanoindentation experimental results of nickel coatings produced from emulsion with supercritical carbon dioxide (Sc-CO_2) showed that the hardness increased gradually from about 1.75 GPa in the brass substrate matrix to about 9.25 GPa in the Ni coatings, which was by 30% higher than that of conventional electroplating Ni coatings. The improvement of Young’s modulus of Ni coatings produced from emulsion with Sc-CO_2 was around 10%. The change in high hardness and strength was considered to relate to the change of grain size. Thus the new Ni coating film has high hardness, low rigidity and high stiffness. This tendency of low rigidity with high stiffness corresponds to the quality of the amorphous metal. This feature refers that the properties of noncrystalline Ni coating film with grain size of 10 nm are very close to the amorphous structured metal properties. Thus, this method producing nanostructured coating film with high deformation resistivity can be applied for new tribological component development.

6. ACKNOWLEDGEMENT

The authors would like to express their thanks to Mr. Kenichiro Chuma for his cooperation during the nanoindentation tests.

7. REFERENCES

1. Madou, M., 1999, *Fundamental of Micro Fabrication*, CRC Press, Boca Raton, FL.
2. Reza, A. M. and Padma, P., 2004, “Nano indentation of nanocrystalline Ni with geometrically different indenters”, Material Science and Engineering A, 372:252-260.
3. Luo, J. K., Flewitt, A. J., Spearing, S. M., Fleck, N. A and Milne, W. I., 2004, “Young’s modulus of electroplated Ni thin film for MEMS applications”, Materials letters, 58:2306-2309.
4. Tuck, J. R., Korsunsky, A. M., Davidson, R. I., Bull, S. J. and Elliott, D. M., 2000, “Modelling of the hardness of electroplated nickel coatings on copper substrates”, Surface and Coatings Technology, 127:1-8.
5. Yoshida, H., Sone, M., Mizushima, A., Abe, K., Tao, X. T., Ichihara, S. and Miyata, S., 2002, “Electroplating of Nanostructured Nickel in Emulsion of Supercritical Carbon Dioxide in Electrolyte Solution”, Chemistry Letters, 11: 1086-1087.
6. Yoshida, H., Sone, M., Wakabayashi, H., Yan, H., Abe, K., Tao, X. T., Mizushima, A., Ichihara, S. and Miyata, S., 2004, “New electroplating method of nickel in emulsion of supercritical carbon dioxide and electroplating solution to enhance uniformity and hardness of plated film”, Thin solid films, 446:194-199.
7. Wakabayashi, H., Sato, N., Sone, M., Takada, Y., Yan, H., Abe, K., Mizumoto, K., Ichihara S., and Miyata, S., 2005, “Nano-grain structure of nickel

films prepared by emulsion plating using dense carbon dioxide", Surface and Coatings Technology, 190:200-205.

8. Mizushima, M., Sone, M., Yan, H., Nagai, T., Shigehara, K., Ichihara, S. and Miyata S., 2005, "Nanograin deposition via an electroplating reaction in an emulsion of dense carbon dioxide in a nickel electroplating solution using nonionic fluorinated surfactant", Surface and Coatings Technology, 194:149-156.
9. Rahman, M. Z., Sone, M., Eguchi, M., Ikeda, K., Miyata, S., Yamamoto, T., 2004, "Wear properties of nickel coating film prepared by emulsion of dense carbon dioxide", *Proc. 3rd Int. Sympo. on Tribology of Vehicle Transmission*, pp. 248-251.
10. Oliver, W. C. and Pharr, G. M., 1992, "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments", Journal of Materials Research, 7:1564-1583.
11. Kumar, K. S., Suresh, S., Chisholm, M. F., Horton, J. A., Wang, P., 2003, "Deformation of electrodeposited nanocrystalline nickel", Acta Materialia, 51: 387–405.